

Stream chemistry modeling of two watersheds in the Front Range, Colorado

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Abstract. We investigated the hydrologic, geochemical, and biogeochemical controls on stream chemical composition on the Green Lakes Valley and Andrews Creek watersheds using the alpine hydrochemical model (AHM). Both sites had comparable data sets from 1994 and 1996, including high-resolution spatial data and high-frequency time series of hydrology, geochemistry, and meteorology. The model of each watershed consisted of three terrestrial subunits (soil, talus, and rock), with the routing between the subunits determined by spatial land cover data. Using 1994 data for model calibration and 1996 data for evaluation, AHM captured the dominant processes and successfully simulated daily stream chemical composition on both watersheds. These results confirm our procedure of using spatial and site-specific field and laboratory data to generate an initial catchment model and then calibrating the model to calculate effective parameters for unmeasured processes. A net source of nitrogen was identified in the Andrews Creek watershed during the spring snowmelt period, whereas nitrogen was immobilized in the Green Lakes Valley. This difference was most likely due to the larger and more dominant area of talus in the Andrews Creek watershed. Our results also indicate that routing of snowmelt through either soil or talus material is sufficient for retention of H⁺ and release of base cations but that N retention is more important on areas mapped as soil. Owing to the larger ionic pulse and larger fraction of surface runoff the Green Lakes Valley was more sensitive to a doubling of wet deposition chemistry than the Andrews Creek watershed.

1. Introduction

The thin soils, limited vegetation, and snow-dominated hydrology of alpine regions limit their ability to buffer against changes in climate and atmospheric deposition [Melack and Stoddard, 1991]. In the Front Range of Colorado the predicted response of alpine watersheds to changes in climatic and chemical inputs has implications for the health of aquatic resources and the setting of emissions standards [Williams *et al.*, 1996]. Owing to their close proximity to urban sources of air pollution, alpine catchments in the Colorado Front Range are subjected to increased atmospheric deposition [Williams *et al.*, 1996] and are already undergoing N saturation, a process where previously N-limited systems begin to leak inorganic nitrogen [Aber, 1992; Williams *et al.*, 1996]. More recently, it has been hypothesized that areas of talus and the material buried beneath talus are responsible for the high NO₃⁻ concentrations observed in early spring snowmelt and the high

summertime concentrations observed in the streams of the Front Range [Williams *et al.*, 1997; Baron and Campbell, 1997]. Furthermore runoff flow path exerts a large control on the stream chemistry and on the response to chemical perturbations of a watershed [Grosbois *et al.*, 1988; Campbell *et al.*, 1995; Brown, 1998].

The alpine hydrochemical model (AHM) was specifically designed to investigate the problem of episodic acidification in alpine watersheds. AHM differs from several other watershed acidification models, such as the model of acidification of groundwater in catchments (MAGIC), that were designed with longer time steps to address questions of chronic acidification [Cosby *et al.*, 1985]. The problem of episodic acidification is especially important in alpine watersheds because of the ionic pulse of chemicals in the snowpack and the fact that even changes in watershed acidity of only 3 days can have an impact on the aquatic biota of alpine watersheds [Barmuta *et al.*, 1990]. The AHM uses a conceptual representation of watershed hydrologic and biogeochemical processes that differs from empirical approaches that have been developed for investigating regional sensitivity to episodic acidification [Eshleman *et al.*, 1995; Leydecker *et al.*, 1999]. This conceptual structure permits the investigation of the processes and watershed properties that determine watershed sensitivity to acidification. Areas of modeling uncertainty can be used to guide field research and improve our understanding of alpine hydrologic and biogeochemical processes.

The alpine hydrochemical model (AHM) was developed in part to improve our understanding of how alpine watersheds will respond to perturbations [Wolford *et al.*, 1996]. AHM was initially used to simulate the hydrochemistry of the 1.2-km²

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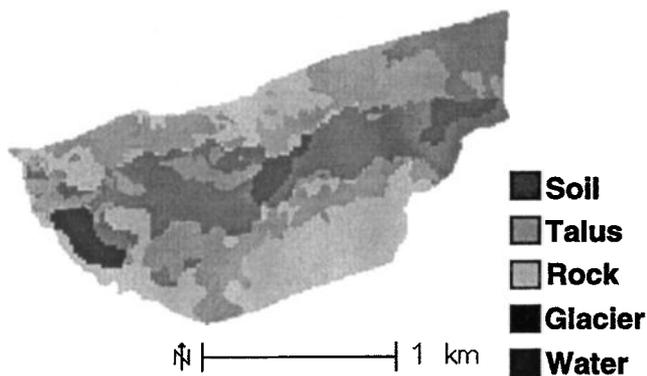


Figure 1. Land cover map for Green Lakes Valley watershed.

Emerald Lake watershed in the Sierra Nevada of California [Wolford *et al.*, 1996] and has since been applied to two watersheds near Emerald Lake [Meixner *et al.*, 1998]. Extension of the AHM to other alpine catchments will improve both our confidence in the model and our understanding of biogeochemical processes.

We applied the AHM to the Andrews Creek and Green Lakes Valley watersheds of the Rocky Mountain Front Range to address four questions. First, can the AHM describe the stream chemistry of these two watersheds using a similar description of chemical processes as was used earlier to simulate the Emerald Lake watershed in the Sierra Nevada? Second, what differences in nitrogen dynamics exist between these two catchments, and how can the AHM be used as a tool to investigate these differences? Third, since the physical relationship between soil, exposed bedrock, and talus differs between these two watersheds, what role does flow routing have in determining the hydrochemical response of alpine watersheds? Finally, how do the models of these two watersheds differ in their sensitivity to changes in atmospheric deposition?

2. Methods

2.1. Site

Green Lakes Valley and Andrews Creek are alpine watersheds in the Front Range of the Rocky Mountains. Green Lakes Valley [Caine, 1995] is part of the Niwot Ridge long-term ecological research site (LTER), and Andrews Creek [Baron and Mast, 1992] is part of the United States Geological Survey (USGS) Water, Energy, and Biogeochemical Budgets Program. In the Green Lakes Valley, water quality for eight different locations along the first-order stream in the valley has been monitored since 1981. GLV4, the upper 2.2 km² of the 7-km² Green Lakes Valley, represents the alpine portion of the larger catchment. GLV4 ranges in elevation from 3550 m at the outflow from Green Lake 4 to over 4000 m at the continental divide with relatively equal areas of rock (30%), talus (36%), and soil (30%) (Figure 1). The remaining 4% of the watershed is covered by Green Lakes 4 and 5. The soil in the Green Lakes Valley is located along the valley floor and is adjacent to the stream. The areas of talus are generally located up hill from the valley and drain into the soil. The areas of exposed rock in the watershed are located most prominently along the tops of ridges [Brown, 1998].

Andrews Creek, a catchment nested within the Loch Vale

watershed, ranges in elevation from 3200 to 4000 m and has an area of 160 ha. The watershed is dominated by rock (57%) and talus (31%) (Figure 2). In contrast to the Green Lakes Valley, soils (11%) are confined to a few areas of tundra and wetland soils on the ridge line of the watershed and at the base of the watershed [Walthall, 1985]. Areas of talus dominate the valley bottom and are adjacent to Andrews Creek.

The two watersheds share a common lithology of silver plume granite and biotite gneiss [Cole, 1977; Pearson, 1980]. The hydrology of both watersheds is dominated by a large wintertime snowpack that melts during the spring and summer and frequent summer precipitation [Caine, 1995; Baron and Mast, 1992]. Both watersheds have no deep groundwater storage, and with the small volume of soil present in the watersheds, there is little soil zone storage.

Both watersheds are drained by a single first-order stream. Stream water discharge is monitored continuously at a gauging station at the base of each watershed. Stream water samples are collected for chemical analysis at the same locations. Both watersheds are topped by glaciers: the 8-ha Arikaree glacier of GLV4 and the 10-ha Andrews glacier of the Andrews watershed.

2.2. Model Structure

The AHM [Wolford *et al.*, 1996] is a lumped conceptual model that was designed for simulating the hydrology and biogeochemistry of alpine watersheds. Modeling a watershed with the AHM requires that a particular structure be chosen to describe the hydrologic and biogeochemical cycles of a watershed. The GLV4 and Andrews Creek watersheds were broken down into three terrestrial subunits (soil, rock, and talus), with a single stream subunit. The area and spatial relationships of soil, rock, and talus were determined from digitized soils maps [Brown, 1998; Walthall, 1985]. For GLV4, flow from the rock subunit was routed onto talus and routed from there to the soil subunit before entering the stream. For Andrews, runoff from the rock and soil subunits was routed to talus and routed from there to the stream.

Each terrestrial subunit contains different compartments representing the snowpack, snowpack-free water, snowmelt, surface runoff, interception by trees and litter, and zero, one, or multiple soil horizons. Stream subunits consist of different

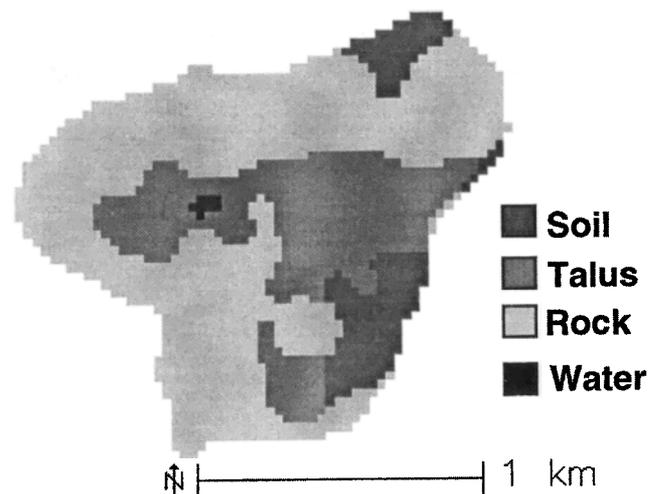


Figure 2. Land cover map for Andrews Creek watershed.

compartments representing the snowpack, snowpack-free water, snowmelt, stream ice, and streamflow (Figure 3). In addition to the compartments described for the stream, lake subunits can be stratified with the two lake layers varying in thickness. Hydrologic processes are modeled separately from geochemical processes.

At each daily time step, AHM adjusts snow-covered area, computes interception, adjusts snowpack for precipitation and melt, calculates influxes of materials to each soil and rock subunit, drains surface runoff, computes evapotranspiration and sublimation, calculates kinetic reactions, calculates chemical equilibrium in soil compartments, drains water from the soil horizon, calculates chemical equilibria in streams, and produces output. Chemical speciation is handled using equations adapted from MINEQL [Westall *et al.*, 1976]. One strength of the model is its precise mass and charge balance for both chemical species and hydrologic calculations [Wolford *et al.*, 1996].

2.3. Model Inputs

Many model inputs for GLV4 were taken directly from data downloaded from the Niwot Ridge LTER web site (<http://culter.colorado.edu:1030/>). For Andrews, data were collected and distributed as part of ongoing USGS efforts to study biogeochemical budgets in the Loch Vale watershed [Baron and Campbell, 1997]. Inputs to the model include potential evapotranspiration (PET), potential sublimation (PS), snow-covered area (SCA), and precipitation quantity and quality.

Mean evapotranspiration from field measurements was used for both catchments. During winter, PET was set to 0.66 mm d⁻¹ and was set to 1.3 mm d⁻¹ during the summer. PS was set to 75% of these values based on experience from modeling evaporation at Emerald Lake [Wolford, 1992]. The model calculates actual evaporation from soil and talus surfaces based

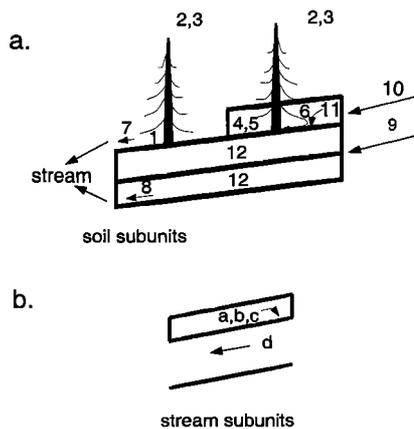


Figure 3. Modeled watershed compartments. (a) Soil subunits have compartments including (1) rainfall litter interception, (2) snowfall canopy interception, (3) rainfall canopy interception, (4) snowpack, (5) snowpack-free (liquid) water, (6) snowpack drainage, (7) surface runoff leaving the subunit, (8) soil drainage leaving the subunit, (9) contributed soil drainage, (10) contributed surface runoff, (11) litter storage beneath the snowpack, and (12) one or more soil horizons. Rock subunits (not shown) do not include compartments 2, 3, 8, and 12. (b) Stream subunits have compartments including the snowpack, snowpack-free water, snowpack drainage (a, b, and c respectively), and streamflow (d); stream ice is not tracked other than present or absent.

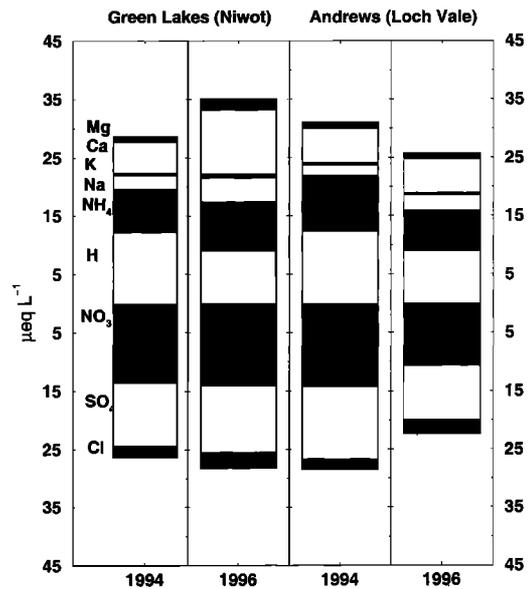


Figure 4. Annual average volume weighted mean precipitation chemistry for GLV4 and Andrews for 1994 and 1996. Data were collected at NADP sites located near each watershed.

on a parameter that defines the fraction of PET that actually evaporates. (For this application, evaporation from soil was equal to PET, and evaporation from talus was 0.9 of PET.)

Ingersoll [1995] developed a 1994 SCA time series for Andrews. Additional SCA maps were developed from orthorectified air photos of the Green Lakes Valley in 1994 and 1996 and Andrews in 1996. For early dates (April 22, 1994, and May 9, 1996), shaded areas were masked out during classification and classified separately. These maps were evaluated using visual inspection, and classification was repeated until a good visual match resulted. SCA maps were overlaid with soils maps to determine SCA for each subunit [Brown, 1998; Walthall, 1985]. Glaciers were assumed to overlie talus.

For GLV4, precipitation quantity was recorded continuously at the Niwot Ridge LTER D-1 meteorological station at the edge of the watershed (elevation 3743 m). The gauge is shielded by a snow fence and an alter shield to improve estimates of precipitation during windy periods. Precipitation events were classified as rain if mean daily temperature was above 0°C. Precipitation chemistry is sampled weekly 2.2 km to the east of D-1 at the Niwot Ridge Saddle Tundra Laboratory as part of the National Atmospheric Deposition Program/National Trends Network [Peden, 1992] (see also National Atmospheric Deposition Program (NRSP-3)/National Trends Network, Coordination Office, Illinois State Water Survey, 1998, <http://nadp.sws.uiuc.edu/>) (hereinafter referred to as NADP/NTN, 1998) (Figure 4).

For Andrews, precipitation quantity was recorded continuously with two Belfort rain gauges at a meteorological station in the nearby main valley of Loch Vale watershed (elevation 3160 m). One gauge has a nipher wind shield, and the other has an alter wind shield. Previous studies have shown no significant difference between the two, and they are used interchangeably to produce the most continuous record [Baron and Campbell, 1997; Bigelow *et al.*, 1990]. Precipitation chemistry is sampled weekly at the same location as part of the NADP/NTN (1998) (Figure 4).

Table 1. Soil Physical Properties

Property	GLV4		Andrews	
	Talus	Soil	Talus	Soil
Area, ha	81.3	68.0	51.21	17.82
ρ_b , g cm ⁻³	1.1	1.3	1.1	1.3
Depth, m	0.25	0.30	0.26	0.30
K_{sat} , cm d ⁻¹	400	400	400	400

GLV4 is the upper 2.2 km² of Green Lakes Valley.

Two methods were used to estimate dry deposition to these watersheds. Winter dry deposition for all species was calculated by subtracting winter wet deposition from peak accumulation snow pits. Modeled summer N dry deposition used the estimate of *Baron and Campbell* [1997] which was 1.3 kg ha⁻¹ yr⁻¹. All other species were left at the values used for the Emerald Lake watershed [*Wolford*, 1992].

2.4. Parameter Estimation and Initial Conditions

Using the model structure defined by *Wolford et al.* [1996], field and laboratory measurements were used to set most parameters and initial conditions, with remaining parameters estimated by model calibration using 1994 stream chemistry data. Soil extent, depth, and bulk density were based on soil surveys [*Brown*, 1998; *Litaor*, 1985; *Baron and Mast*, 1992] (Table 1). Mineral weathering rates based on a mass balance of the entire Loch Vale watershed were used for both watersheds [*Mast et al.*, 1990] (Table 2). Exchange coefficients and hydraulic conductivity parameters for the soil and talus were set to the values for the Emerald Lake watershed. Depth-weighted averages of exchangeable ion amounts in soil were estimated using data from *Litaor* [1985] and *Walshall* [1985]. Exchangeable cations for talus and soil in GLV4 were assumed to be identical since no data were available for talus. For Andrews, data for Entisols were used for the talus, and values for Inceptisols were used for the soil subunit in Table 3. Parameters controlling sulfate adsorption were based on data from Loch Vale [*Baron et al.*, 1992], with a sulfate adsorption capacity of 0.71 mmol kg⁻¹ soil. Silica adsorption properties were based on values from the Emerald Lake watershed [*Wolford et al.*, 1996]. Glaciers were assumed to have a depth of 0.1 m of snow water equivalence (SWE) at the beginning and end of the water year to allow for carryover of SWE from year to year and to permit the identification of ablation or accumulation of the glacier.

2.5. Calibration

Model calibration involved three steps: (1) snowmelt optimization, (2) chemical calibration, and (3) optimization of hydrologic parameters [*Meixner et al.*, 1998]. Snowmelt optimization estimated daily melt rates by subunit using SCA and discharge to constrain the search for optimal snowmelt rates. As annual discharge exceeded measured precipitation less es-

Table 3. Soil Chemical Properties

Property	Andrews Talus	Andrews Soil	GLV4
CEC ^a , meq kg ⁻¹	67	76	138
PBS ^b , %	52	70	85
Ca ²⁺ ^c , meq kg ⁻¹	27.5	38	102
Mg ²⁺ ^c , meq kg ⁻¹	4.1	13	11.6
K ⁺ ^c , meq kg ⁻¹	1.7	1.6	2.6
Na ⁺ ^c , meq kg ⁻¹	1.4	1.0	0.8

^aCEC is cation exchange capacity, expressed in milliequivalent of charge per kilogram of soil.

^bPBS is percent base saturation, the percent of the total CEC that is occupied by base cations as opposed to hydrogen ion or aluminum ions.

^cThis is the quantity of exchangeable ion, by species, in the soil.

timated evaporation, snow was added to both watersheds in both years to achieve mass balance.

Calibration proceeded as a stepwise adjustment of chemical parameters until model output matched observations (Table 4). First, the ionic pulse parameter (D) was adjusted to fit stream Cl⁻. Second, cation exchange coefficients were adjusted for each cation until modeled soil concentrations matched target values. Third, SO₄²⁻ adsorption parameters were changed to increase or decrease modeled SO₄²⁻ concentrations in the soil and stream. Fourth, parameters governing N consumption in the soil were altered to improve the fit to stream NO₃⁻ and NH₄⁺ concentrations. N parameters were set at the beginning of each calendar month and remained constant for the entire month. Finally, mineral weathering rates and silica adsorption parameters and initial conditions were adjusted to capture the observed Si concentrations. If necessary, hydrologic parameters were changed to improve simulations. Model evaluation was done using inputs and stream chemistry for 1996.

Calibration decisions and evaluation judgments were made by visually comparing modeled stream time series with the available observations. For the purposes of comparison the Nash-Sutcliffe statistic (coefficient of efficiency) was calculated for the initial (uncalibrated) and calibrated models for both watersheds for 1994 and 1996 for all species and hydrologic discharge. The Nash-Sutcliffe value is calculated as

$$E = 1.0 - \frac{\sum_{i=1}^n (O_i - P_i)^2}{\sum_{i=1}^n (O_i - \bar{O})^2}, \quad (1)$$

where P is the predicted value, O is the observed value, \bar{O} is the mean observed value, and i is the observation number. A value of E less than zero indicates that the mean of the observations is a better predictor of the observed data than the

Table 2. Mineral Weathering Rates

Properties	H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	SiO ₂	SO ₄ ²⁻	Anion
Annual export, mol yr ⁻¹	7380	21310	6070	11800	3440	27050	1970	19350
Daily export, mol d ⁻¹	20.211	58.4	16.6	32.34	9.43	74.1	5.39	53
k_2 , 3 mol d ^{-1.0} m ^{-2.0}	0.586	1.69	0.481	0.91	0.274	2.15	0.156	1.53

^aHere k_2 is model stoichiometric parameter, and it defines the mol d⁻¹ of a given species that weather when multiplied by soil volume, soil bulk density, and specific surface area.

model. Higher values (closer to 1) indicate better agreement between the model and observations [Nash and Sutcliffe, 1970; Wilcox et al., 1990; Legates and McCabe, 1999].

3. Results

3.1. Green Lakes Valley

Optimization of water inputs and snowmelt achieved a near perfect match between measured and modeled discharge except for a few large rainfall events during the summer (Figure 5). Measured snowfall at D-1 in the 1994 water year was 1.05 m, while the model input was 1.11 m. In 1996, measured snowfall at D-1 was 1.00 m versus a model input of 1.35 m.

Little calibration was needed to improve the match between measured and modeled stream concentrations, with soil chemical parameters being most important. A total of 13 chemical parameters were adjusted from their original Emerald Lake watershed (ELW) values during the calibration (Table 4). Adjusting hydrologic parameters, altering model structure, and adjusting parameters controlling talus processes did not significantly improve modeled stream chemical concentrations. Af-

Table 4. Fitted Parameter Values

Parameter	ELW	Andrews ^a	GreenLake 4 ^a
Deep K_{sat}^b , cm d ⁻¹	1.25	10.25	1.25
Log P_{CO_2} , stream (atm)	-2.9	-3.4	-3.1
Snowpack elution parameter D^c	4.0	3.4	8.0
Talus log $K-Ca^{2+d}$	-6.15	-5.63	-6.15
Talus log $K-Mg^{2+d}$	-6.00	-5.83	-6.00
Talus log $K-K^{+d}$	-1.00	-1.30	-1.00
Talus log $K-Na^{+d}$	-2.95	-2.15	-2.95
Soil log $K-Ca^{2+d}$	-5.23	-5.23	-4.83
Soil log $K-Mg^{2+d}$	-5.73	-5.73	-5.03
Soil log $K-K^{+d}$	-0.85	-0.85	-1.20
Soil log $K-Na^{+d}$	-3.01	-3.01	-2.11
Log $K-SO_4^{2-c}$	17.45	17.95	17.70
Log $K-Si^e$	27.63	27.93	27.88
Exchangeable Si ^f	95	90	70
aNH3toON ^g	0.989	0.000	0.200
aNO3toON ^g	0.70	0.5	0.5
NO_3^- - base ^g	8×10^{-6}	5×10^{-5}	3×10^{-5}
α^h	0.16	0.16	0.18

^aFor Andrews Creek, soil parameters had no effect on model output. For Green Lakes Valley, talus parameters had no effect on model output. This result is discussed more extensively in the text.

^bDeep hydraulic conductivity refers to lower horizon hydraulic conductivity.

^cThis represents ratio of initial solute concentration in snowmelt to snowpack average. All other elution parameters were unchanged from Emerald Lake watershed (ELW).

^dLog K for exchange of cation with H^+ on cation exchange site.

^eLog K for adsorption of SO_4^{2-} and H_2SiO_3 .

^fThe model contains a Si exchange complex. The numbers in this row refer to initial condition of complex by percent saturation of exchange sites. Total site concentrations from ELW optimization were used here.

^gThese three parameters govern the two N reactions present in AHM: $NH_4^+ \leftrightarrow \text{organic N} + H^+$ and $NH_4^+ + 2O_2 \leftrightarrow NO_3^- + 2H^+$. The aNH3toON determines what percent of the NH_4^+ is converted into organic N with the remainder being nitrified. NO_3^- -base determines a minimum concentration of NO_3^- over which a fraction of the NO_3^- as governed by aNO3toON is converted into organic N.

^hThe weathering coefficients α is part of the weathering equation: $\text{mol} = A \times k \times [H^+]^\alpha$, where mol is moles added to the subunit, A is total area of the surfaces involved in reactions, $[H^+]$ is hydrogen ion concentration, and k and α are constants. The total surface area is determined as the product of the soil depth, area, bulk density, and specific surface area.

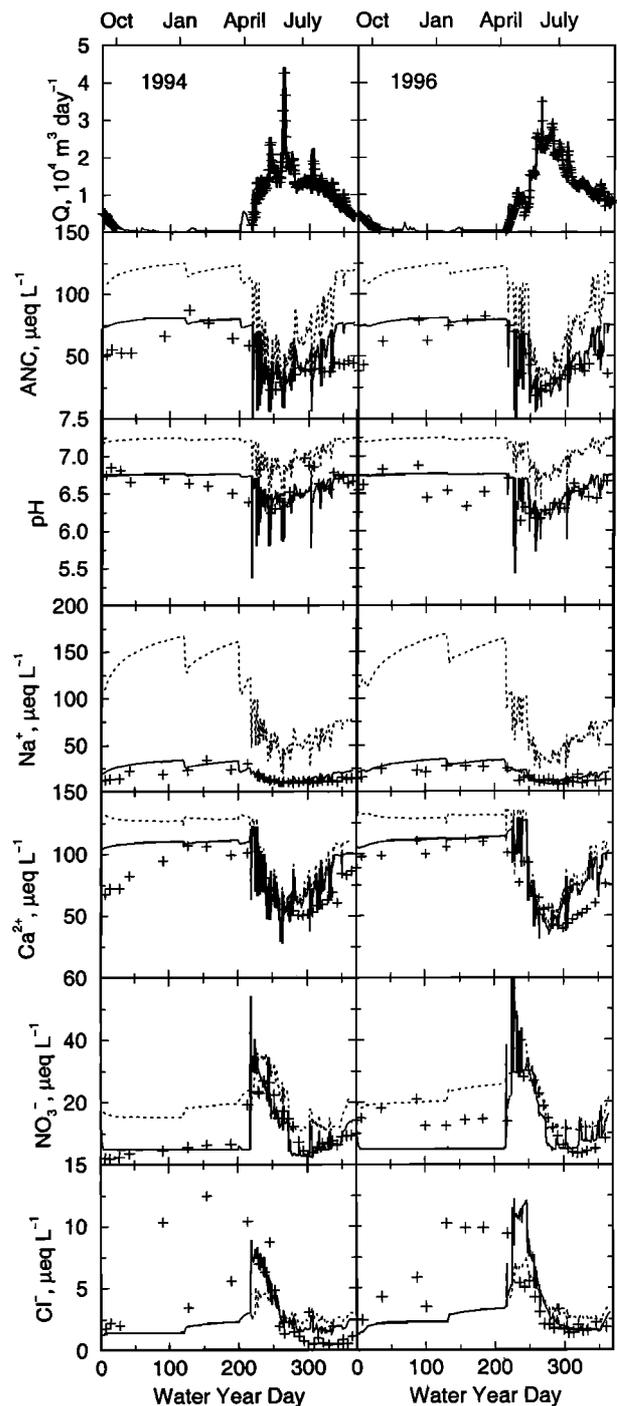


Figure 5. Modeled Green Lake 4 (GL4) inflow and measured stream chemical concentrations for the outflow of Green Lake 4. Solid curve is final calibrated model, pluses are data, and dashed curve is uncalibrated model using field and Andrews results for model parameter values. Water year day 1 is October 1.

ter calibration the match of model output to measured stream concentrations was improved for much of both calibration and evaluation years (Figure 5 and Table 5). Model results show day to day variability not present in the data due in part to sampling interval and in part to comparing modeled stream to observed lake outflow.

The best matches of modeled and measured stream concen-

Table 5. Nash-Sutcliffe Values for Green Lakes Valley 4

Species	1994		1996	
	U	C	U	C
ANC	-7.7	-0.32	-3.32	0.49
Ca ²⁺	-1.3	0.22	0.12	0.59
Cl ⁻	-0.20	-0.01	-0.02	-0.31
K ⁺	-1.2	-0.38	-0.74	0.16
Mg ²⁺	-27.5	0.25	-13	0.63
Na ⁺	-150	0.12	-130	0.28
NH ₄ ⁺	-0.45	-0.44	-0.88	-0.88
NO ₃ ⁻	0.23	0.74	0.36	0.35
H ⁺	-1.7	0.065	-1.9	-1.3
Discharge	0.97	0.98	0.99	0.99
Si	-2.7	0.015	-0.37	-0.086
SO ₄ ²⁻	-43.1	-0.71	-12	0.53

U is uncalibrated; C is calibrated.

trations were for ANC, pH, and Na⁺. Only after water year day (WYD) 320 (August 20) was ANC overpredicted, with a small underprediction at the initiation of snowmelt (around WYD 215, May 1). Na⁺ predictions were very good, especially when compared to the initial model run, with some overprediction after WYD 324 (August 20).

Predictions for Ca²⁺ were not as good as for Na⁺. Early to midwinter (WYD 1–150, October 1 to March 1) concentrations are overpredicted by the model, while melt season (WYD 200–253, April 20 to June 10) concentrations are underpredicted. In general, the matches between modeled and observed SO₄²⁻, Mg²⁺, and K⁺ (not shown) were very good for the 1994 simulation, and simulation difficulties were similar to those for Ca²⁺.

The monthly calibration of nitrogen parameters resulted in a very good fit between measured and modeled NO₃⁻ concentrations. Modeled values were somewhat higher than observed during the initial stages of snowmelt (around WYD 213, May 1) for both 1994 and 1996. This is most likely due to the high value used for snowpack elution (Table 4). The high value for the elution parameter was necessary in order to capture the high Cl⁻ concentrations in 1994 and avoid overpredicting the late summer concentrations. However, the high value for the elution parameter also resulted in faster than observed Cl⁻ release from the snowpack in 1996. We were unable to match the observed Cl⁻ concentrations in the first half of the water year using this model structure.

3.2. Andrews Creek

The meteorological station estimate of snowfall was 0.78 m and 0.98 m for 1994 and 1996, respectively, versus model inputs, to meet mass balance requirements, of 1.03 m and 1.28 m. After optimization, there was a near perfect match between measured and modeled watershed discharge, except for following a few large summer rains (Figure 6).

The main improvement to the match between measured and modeled stream concentrations came from adjusting only 12 parameters (Table 4), 11 of which controlled processes in the talus subunit and the other parameter controlling stream P_{CO₂}. Though many of the parameters controlling processes in the soil subunit were adjusted, none significantly improved model performance (Figure 6 and Table 6). Both the mean and variability of the data are simulated well by the calibrated model in both years with the partial exception of NO₃⁻, Si, and ANC. Despite monthly calibrated values of parameters for immobi-

lizing NH₄⁺ and NO₃⁻, the spring snowmelt portion of the simulation (between WYD 222 and 274, May 10 to July 1) underpredicts NO₃⁻ concentrations.

The model captured the mean ANC for the season but not the seasonal trend of ANC. Early season predictions (before WYD 250, June 10) are too low, while midseason predictions

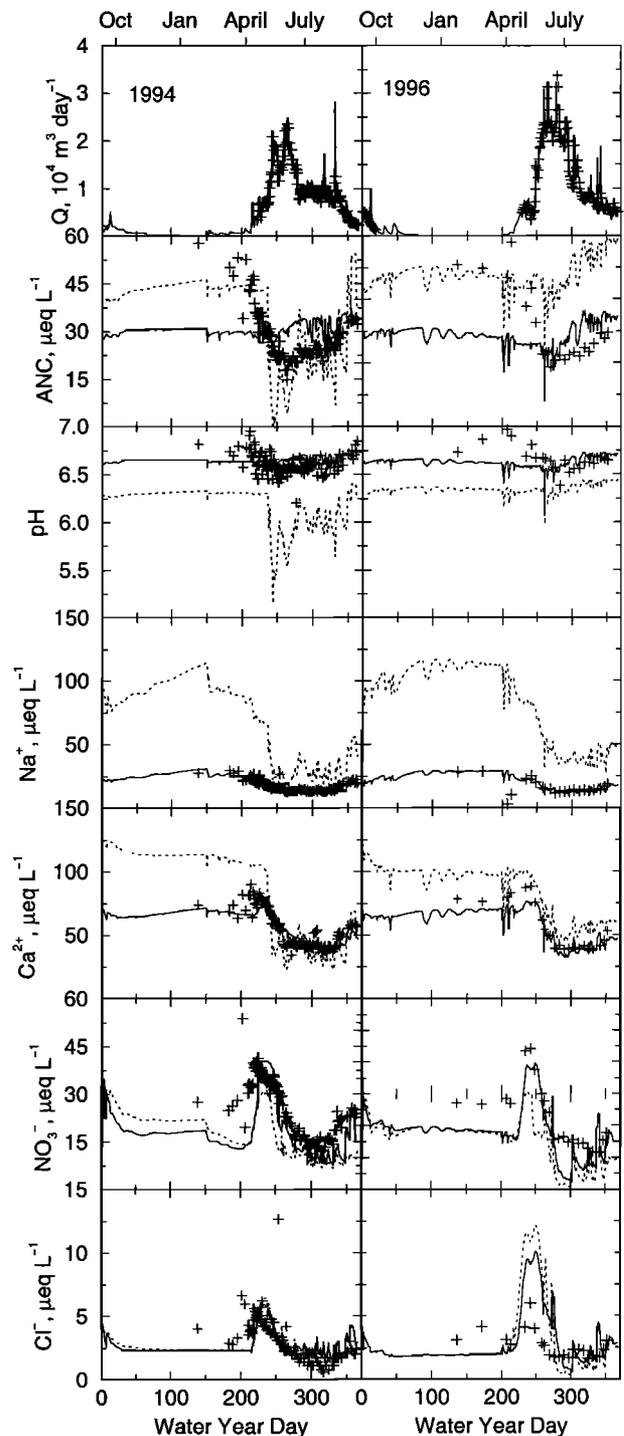


Figure 6. Observed and modeled stream chemical concentrations for the Andrews Creek. Solid curve is final calibrated model, pluses are data, and dashed curve is uncalibrated model using field and Emerald Lake results for model parameter values.

(WYD 250–283, June 10 to July 10) are too high for both 1994 and 1996.

Despite the general agreement between model simulation and observations for Ca^+ , there is still disagreement between model and measured values. The results for Ca^+ typify those of cations and SO_4^{2-} . Early season values are slightly below measured values, and late season predicted values (after WYD 324, August 20) are below measured values (Figure 6).

4. Discussion

4.1. Model Performance

The models of GLV4 and Andrews Creek were effective in capturing the mean and seasonal variability of the observed stream chemistry for both a calibration and an evaluation year. The models were effective by fitting a few parameters and using field data to set model initial conditions, model inputs, and several model parameters. Even though the model construction and calibration can be considered a success, it was a variable one, with some measurements better matched than others by the model.

Discharge was modeled successfully; this was due in large part to the snowmelt optimization scheme. Optimization for GLV4 resulted in 11% and 35% increases in modeled SWE over the amount measured at D-1 for 1994 and 1996, respectively. At Andrews the increases were 25% and 24% for 1994 and 1996, respectively. The need to add additional snow may arise from (1) estimates of evaporation (and sublimation) that are too high, (2) underestimates of snowfall, (3) snow blown into the watersheds from over the Continental Divide, or (4) ablation of the Arikaree or Andrews glaciers. The estimates of evaporation we used are, if anything, too low; the results of *Hartman et al.* [1999] indicated much higher rates of evaporation. More likely, are differences in total precipitation between the two watersheds modeled and the precipitation gauges due to orographic effects. It is also likely that snow is blown into both watersheds from over the Continental Divide [*Baron and Denning*, 1992]. There are no available data concerning the ablation of either the Andrews or Arikaree glaciers during the 1994 and 1996 water years.

There was some overprediction of discharge for several summer storms on both watersheds (Figures 5 and 6), especially the large storms around WYD 300 (July 30) in both 1994 and 1996 on GLV4. For the Andrews Creek watershed in 1994, discharge for the storm after WYD 320 (August 16) was also vastly overpredicted by the model. That particular storm was also greatly overpredicted by *Hartman et al.* [1999] when they simulated discharge for the whole Loch Vale watershed using the regional hydro-ecological simulation system (RHESys) modeling package [*Band et al.*, 1993]. The overprediction of summer rainfall peak discharges may be due to insufficient soil zone storage in both models or using incorrect precipitation measurements as input to the models. The AHM model also overpredicted flows at the beginning of snowmelt, indicating that soil moisture status was not accurately calculated during the midwinter period. Both problems in modeling discharge indicate a need to increase infiltration rates and subsurface water storage in both watersheds.

The AHM was variably successful at predicting stream concentrations during both 1994 and 1996, suggesting that the major processes controlling stream chemical concentrations for both watersheds are captured by their respective models. Information about the model and about the calibration proce-

Table 6. Nash-Sutcliffe Values for Andrews Creek Watershed

Species	1994		1996	
	U	C	U	C
ANC	-0.36	-0.11	-2.0	0.12
Ca^{2+}	-0.40	0.79	0.48	0.90
Cl^-	0.18	0.22	-5.9	-3.6
K^+	-4.1	0.29	-2.0	0.34
Mg^{2+}	-2.0	0.31	-0.44	0.86
Na^+	-50	0.66	-55	0.045
NH_4^+	-0.15	-0.15	-1.3	-1.32
NO_3^-	-0.56	0.06	-1.4	0.52
H^+	-310	-0.056	-7.5	0.14
Discharge	0.98	0.95	-0.92	0.92
Si	-12	-2.5	-3.25	0.04
SO_4^{2-}	-17	0.58	-18.6	0.10

cedure can be garnered from investigating the Nash-Sutcliffe values for GLV4 and Andrews for the calibrated and uncalibrated watershed models as well as by comparing the results for the calibration and evaluation years. The Nash-Sutcliffe values for Ca^{2+} , ANC, K^+ , and Mg^{2+} were closer to 1.0 for the evaluation year of 1996 than they were for the calibration year of 1994 for both watersheds. This result indicates that the calibration was not overly tuned to the observational data from 1994 (Tables 5 and 6). Therefore we can be more confident in our calibration procedure in general and the particular parameter values arrived at in this analysis.

Model predictions for Si, NH_4^+ , and Cl^- in particular were inferior to the observational mean as stream composition predictors (Tables 5 and 6). Silica has an observable hysteresis in stream chemistry of Andrews Creek [*Campbell et al.*, 1995]. This hysteresis may be because of soil solution and talus solution flushing processes not currently incorporated into the AHM models of these two watersheds (D. W. Clow, personal communication, 1999). The observed NH_4^+ concentrations in both watersheds would be difficult for any model to simulate because of the almost random nature of the observed values. Still the AHM currently nitrifies or immobilizes all NH_4^+ in the snowpack on contact with the soil or soil litter. These results indicate that an alternative scheme should be developed. The Cl^- simulations were significantly worse when compared to the mean of the observations for 1996 than they were for 1994. The deterioration of the simulations in the evaluation year of 1996 most likely represents a change in the real ionic pulse between these two years. While Cl^- deposition was higher in both watersheds in 1996 (Figure 3), the overprediction of spring snowmelt stream Cl^- concentration during 1996 indicates that there may be differences in snowpack maturation between the two years [*Harrington and Bales*, 1998]. Unfortunately, there was no detailed snow pit data available to evaluate this hypothesis.

Other problems with the models are only evident by looking at the time series results. For example, late season cation concentrations for GLV4 are overpredicted. Possible causes of this overprediction include (1) high percent soil base saturation in the model, (2) too much soil and talus in the model, or (3) not enough snowmelt routed through the soil, preventing depletion of the cation exchange complex during snowmelt. Of these three possible causes the first is the most likely, since the base saturation values for GLV4 are high for alpine watersheds. The second goes against the hydrologic results for the

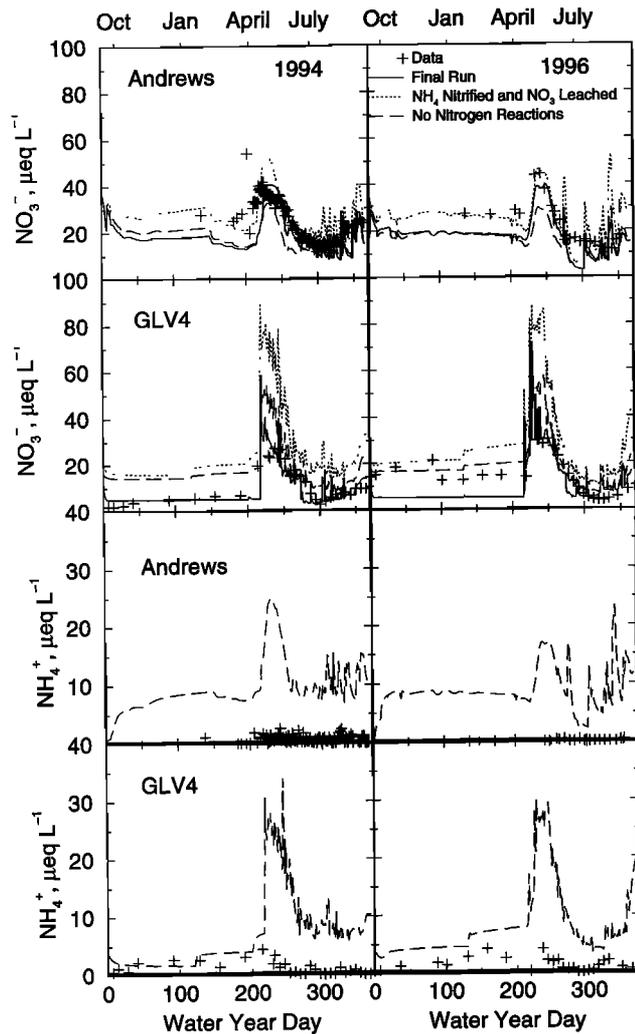


Figure 7. Nitrogen reactions and effects for models of both watersheds.

summer rainfall events, which were overpredicted, indicating that the model needs more not less soil. The third item is plausible since model calculations of soil drainage and surface runoff indicate only 70% of snowmelt comes in contact with soil.

While the Nash-Sutcliffe results indicated a conflict between the magnitude of the ionic pulse between the two years, the time series results indicate an underprediction of winter stream Cl^- at GLV4. This result indicates either a weathering source of Cl^- not included in the model, summer dry deposition of Cl^- at a greater rate than those used, or a pool of evaporated water in the GLV4 that provides the wintertime source of Cl^- .

4.2. Base Saturation and pH

The overprediction of late season stream cation concentrations and the need to increase the stream P_{CO_2} (Table 4) from that of the ambient atmosphere indicate that the base saturation of soils in the model of GLV4 is too high. The GLV4 has a soil base saturation that is 50% greater than the average base saturation in Andrews Creek. Also, the cation exchange capacity of the soils of GLV4 is nearly twice that of Andrews Creek (Table 3). One result of this high cation exchange capacity (CEC) and base saturation is that the pH of soil water, after

degassing to atmospheric P_{CO_2} , will be much higher at GLV4 compared to Andrews Creek. Note the 0.3 pH difference between the calibrated ($P_{\text{CO}_2} 10^{-3.1}$ atm) versus uncalibrated ($10^{-3.4}$ atm) models of GLV4 (Figure 5).

There are several possible causes for the difference between the ambient atmosphere P_{CO_2} and the calibrated P_{CO_2} of the stream. First, the real P_{CO_2} of the samples may be below atmospheric P_{CO_2} because of the grab sample methodology of sample collection. Grab sampling prevents the degassing of CO_2 since a sample is capped immediately, while stream samples taken with an autosampler (like those at Andrews Creek) are allowed to equilibrate with the atmosphere over the days to weeks that the sample sits in the autosampler [Melack *et al.*, 1998]. Second, during winter and early spring, lake ice may prevent the degassing of CO_2 that accumulated because of respiration in the stream and lake. Third, these results may indicate that the base saturation of GLV4 is now much lower than measured in the mid 1980s, because of either errors in measurement or a real decline in base saturation.

Cation concentrations and alkalinity have declined in the streams of Green Lakes Valley [Caine, 1995], a phenomenon that, if occurring more widely in the Front Range, will have policy implications in setting critical loads for atmospheric deposition to the region. The hypothesis that base saturation has declined can be tested by modeling GLV4 farther back in time using stream chemistry data that are available back to 1981, but proxy data would be needed to extend the time series of hydrologic information farther back.

4.3. Nitrogen Dynamics

The model succeeds in matching the NO_3^- concentrations in part because it has been calibrated to match them on a month by month basis. Few conclusions can be drawn from the ability of the model to capture the seasonal variability of NO_3^- ; however, it is useful to see what model output looks like when all NO_3^- is leached and all NH_4^+ is nitrified and when the N reactions are turned completely off (Figure 7). These different sensitivity tests were used to identify and quantify the relative importance of nitrification, mineralization, and immobilization on the stream chemical composition of mineral nitrogen.

The N sensitivity results show that during the early part of the snowmelt season (WYD 230 until 270), nitrification and immobilization are necessary for the model of GLV4 to explain the measured NO_3^- and NH_4^+ concentrations. This result is in contrast to Andrews Creek where AHM modeling indicates a significant source of NO_3^- from the watershed during snowmelt. For NH_4^+ the sensitivity results indicate that nearly all NH_4^+ is assimilated or nitrified on both watersheds. During the summer, observed stream NO_3^- concentrations indicate a significant NO_3^- sink on both watersheds. The summertime peak of N consumption indicates vegetative or soil microbial control of NO_3^- in the GLV4 and Andrews Creek watersheds. There is undoubtedly stream NO_3^- in both watersheds from mineralization and nitrification. Our results indicate that GLV4 has a large N sink that consumes more of atmospheric N deposition than does Andrews. The larger N sink is most likely due to the dominance of soil in the valley bottom of GLV4. Soil is expected to be more biologically active than talus and thus able to retain more N.

4.4. Flow Routing

The results for these two watersheds, combined with those from previous work at Emerald Lake [Wolford *et al.*, 1996] and

two other Sierra Nevada watersheds [Meixner *et al.*, 1998], indicate that most snowmelt contacts either soil or talus long enough to exchange hydrogen ions for cations and to undergo other geochemical transformations. Furthermore, the sensitivity of parameters for a particular terrestrial subunit depends on the flow-routing parameters within the AHM. For GLV4, all runoff was routed through the soil before reaching the stream. At Andrews Creek, all runoff was routed through talus before reaching the stream. At Emerald Lake, half of the stream discharge came from talus, while the other half was from soil. For GLV4 the soil exchange parameters and hydrologic parameters of the talus subunit had no effect on model output, while the soil hydrologic and chemical parameters of the soil subunit were fundamental in determining stream chemical composition. The opposite was true at Andrews. Emerald Lake was intermediate with some talus and some soil parameters important in determining model predictions. These model results indicate that the observed stream chemistry has a similar dependence on the structure of the landscape and the land cover most hydrologically connected to the stream.

Andrews and GLV4 also differ in the fraction of stream discharge that is surface overland flow. Our model results show that there is virtually no surface runoff on the soil and talus in Andrews, while for GLV4 about 30% of total hydrologic flow for the soil and talus subunits occurs as surface overland flow. These differences as well as the differences in flow routing between subunits for the two watersheds highlight the first-order importance of spatial and vertical flow routing to the hydrochemical response of alpine watersheds.

Our results indicate the need for more intensive field measurements of flow routing, including tracer tests, isotopic and geochemical mixing models, soil wetness observations, and soil chemical observations, for determining the actual hydrologic routing in these watersheds. Additionally, more robust watershed hydrologic models, such as TOPMODEL [Beven and Kirby, 1979], should be evaluated as tools to support field observations and to aid in parameterizing flow routing for the AHM.

4.5. Sensitivity to Deposition

Doubling N deposition resulted in small depressions in ANC and pH at GLV4 (Figure 8 and Table 7). The average ANC depression and H^+ increase of 3.4 and $0.1 \mu\text{eq L}^{-1}$, respectively, are similar to the values (3.8 and $0.1 \mu\text{eq L}^{-1}$, respectively) observed for the Emerald Lake watershed under conditions of doubled wet N and SO_4^{2-} deposition [Meixner *et al.*, 1998]. The Andrews Creek watershed model exhibited less sensitivity to increases in atmospheric deposition than GLV4, with ANC depression and H^+ increase of 2.0 and $0.02 \mu\text{eq L}^{-1}$, respectively (Figure 9 and Table 7) [Wolford *et al.*, 1996]. The slightly lower sensitivity of Emerald Lake despite its lower CEC and base saturation is probably due to the very dilute nature of precipitation in the Sierra Nevada. The lower sensitivity of Andrews to increases in deposition is probably due to the significant increase in Ca^{2+} export observed under increased deposition (Table 7) due to the greater contact of deposition with talus than in GLV4.

The maximum concentration change due to doubling wet deposition (Table 7) gives a snapshot of the two watersheds' sensitivity to episodic acidification. The results indicate that GLV4 is more susceptible to episodic acidification than is the Andrews Creek watershed. The maximum ANC depression and H^+ increase for GLV4 were 32.2 and $2.9 \mu\text{eq L}^{-1}$, respec-

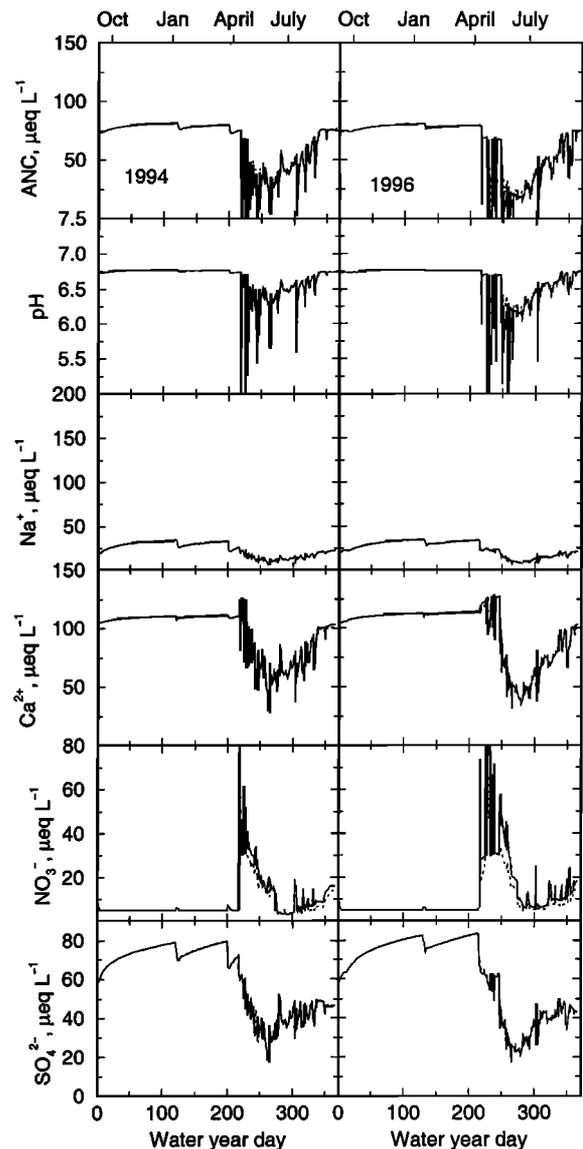


Figure 8. Sensitivity of Green Lake 4 model to doubled nitrogen deposition chemistry. Dotted curve is current conditions, and solid curve is model output for doubled deposition.

tively, while for Andrews they were 7.4 and $0.97 \mu\text{eq L}^{-1}$, respectively. The greater sensitivity of GLV4 to episodic acidification is due to the larger ionic pulse (D value of 10.0) as opposed to Andrews Creek (3.4). The two Rocky Mountain watersheds are more sensitive probably because of the much larger deposition currently occurring.

The finding that GLV4 is more sensitive than the Andrews Creek watershed agrees with the results of Wolock *et al.* [1989]. They found that watersheds with less contact time and more surface runoff were more sensitive to acid deposition. In our case the model of GLV4 had more surface runoff and thus less soil contact than the Andrews Creek watershed. A model test was done in which soil hydraulic conductivity was increased to eliminate surface runoff. Under this scenario (results not shown), GLV4 was less sensitive to increased N deposition than the Andrews Creek watershed. This sensitivity result gives further force to the need for a more robust investigation of flow routing in alpine watersheds.

Table 7. Concentration Changes With Doubling of N Deposition

Species	Average Change				Maximum Change			
	GLV4		Andrews		GLV4		Andrews	
	1994	1996	1994	1996	1994	1996	1994	1996
ANC, $\mu\text{eq L}^{-1}$	-2.3	-4.6	-1.7	-2.4	-32.2	-28.2	-3.5	-7.4
H ⁺ , $\mu\text{eq L}^{-1}$	0.07	0.18	0.014	0.025	0.87	2.9	0.033	0.097
Ca ²⁺ , $\mu\text{eq L}^{-1}$	0.7	0.3	4.7	4.7	8.0	4.1	11.4	12.0
NO ₃ ⁻ , $\mu\text{eq L}^{-1}$	2.6	5.5	8.7	9.7	34.5	35.2	21.3	23.6
SO ₄ ²⁻ , $\mu\text{eq L}^{-1}$	-0.45	-0.20	-0.60	-0.80	-2.9	-1.9	-3.5	-3.8

5. Conclusions

Five lessons were learned from this application of the AHM to the upper portion of the Green Lakes Valley and the Andrews Creek watersheds. First, calibration involving specification of flow routing and measured parameters followed by

fitting of soil and talus parameters that were not explicitly measured was effective in capturing the observed stream chemical composition of the catchments. This procedure should be followed in using AHM to simulate other watersheds. Second, the Andrews Creek watershed releases significantly more mineral N than GLV4. This is especially true during spring snowmelt when the Andrews Creek watershed was a net source of mineral N. The greater release of mineral N is most likely related to the dominance of areas of talus in the Andrews Creek watershed. Third, snowmelt contacts either soil or talus sufficiently long to undergo geochemical transformation. Still, independently parameterized routing is necessary since nitrate retention, apparently biologically related, is more important on areas mapped as soil as opposed to areas mapped as talus. Fourth, GLV4 is more sensitive to changes in atmospheric deposition than the Emerald Lake or Andrews Creek watersheds were on an average and episodic basis. However, this result is dependent upon a confident estimate of flow routing in both of the watersheds. Finally, our results indicate that the soil base saturation estimated from measurements at GLV4 in the mid-1980s is higher than supported by the model of stream composition developed here. This result suggests that the base saturation of GLV4 soils was either not measured properly in the 1980s or that soil base saturation has decreased over the past 15 years.

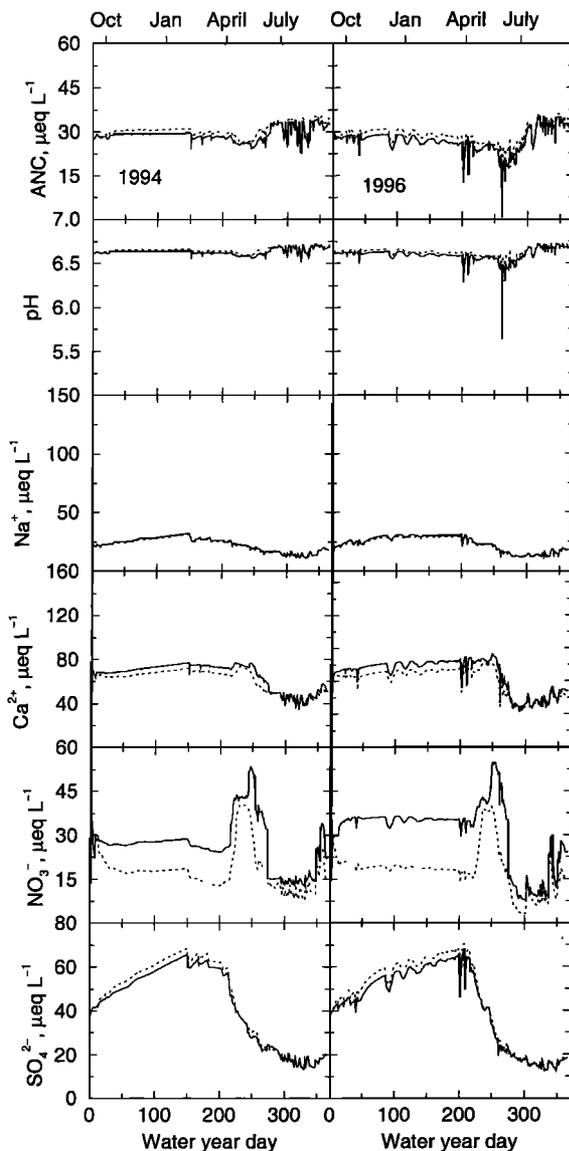


Figure 9. Sensitivity of Andrews watershed model to doubled nitrogen deposition chemistry. Dotted curve is current conditions, and solid curve is for doubled deposition.

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